High-Temperature Research

SINCE the development of the heat engine in the eighteenth century, there has been a continuous search for materials capable of withstanding higher and higher temperatures. Within the past decade, however, this search has been sharply intensified and has taken on greater significance than ever before. Great advances have been made in high-speed flight, rocket propulsion, missile development, atomic reactors, and power plants; meanwhile, industry has gone to high-temperature production and products. These developments have brought about a sudden shift in operational temperatures from a region well below 1,000° C into a range—2,000° to 4,000° C and above—in which there has been little or no previous scientific or industrial experience. As a result, American science and technology are now faced with overwhelming requirements for new basic data, new materials, new instrumentation, new standards, and new measurement techniques. The need is so great, in fact, that further advances are being delayed by a critical lack of basic scientific knowledge in these temperature regions.

Above 1,000° C very few useable data are available; at 2,000° and 3,000° C there is a serious lack; at higher temperatures there is a complete void. Presently available lower-temperature information is of little value above 1,000° C because one cannot safely predict higher-temperature behavior and properties of materials on the basis of experience at normal temperatures. At high temperatures, impurities may have a pronounced effect, totally unexpected complex molecules may be formed, and complete reversals of normal properties may be observed. In the region of highest temperatures—above 4,000° C—the general lack of data is accompanied by a lack of adequate temperature scales, adequate measurement devices, and comprehensive theoretical concepts.

Thus, to measure, describe, and explain the behavior of materials at the higher temperatures, new concepts, techniques, and instrumentation must be developed which in themselves may constitute almost a new branch of physical science. Urgently needed, for example, is information on the thermodynamic proper-

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SPECIAL HIGH-TEMPERATURE ISSUE

In view of the current widespread interest in high-temperature research, two successive issues of the Technical News Bulletin are being devoted to this subject. This issue contains articles on the structure and properties of high-temperature materials; the July issue will deal with high-temperature measurements.

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ties of materials in solid, liquid, and gaseous states over a very wide temperature range—from 0° to 6,000° or 8,000° K—and over a pressure range from 1 to 10,000 atm. Data are also greatly needed on chemical reaction rates and mechanisms and on rates for various physical processes at higher temperatures. In heat and mass transfer and in fluid dynamic calculations, information is required on transport properties such as viscosity, thermal conductivity, and diffusion. For the correlation, theoretical analysis, and computation of high-temperature properties, molecular and crystal structure data are required such as X-ray and electron diffraction patterns and Raman, infrared, microwave, and electronic spectra. Also, suitable statistical-mechanical and quantum-mechanical methods must be developed, particularly in regions of temperature and pressure where direct measurement of thermodynamic and other properties is not feasible.

Until quite recently the work of the National Bureau of Standards in these areas was largely confined to the

To learn more about the structure of materials at high temperatures, extensive use is made of such techniques as X-ray and electron diffraction, electron microscopy, and infrared spectroscopy. Of particular interest for many high-temperature applications are the transformations in structure and properties that occur in materials as the temperature rises. A number of carefully coordinated investigations deal with changes of this kind (see High-Temperature Transformations, p. 104 of this issue; also Viscosity Measurements Above 2,000° C, p. 103).

The second general area is concerned, to a very large extent, with the thermodynamic properties of a variety of potentially useful materials for such applications as aircraft fuels, container materials, or heat-transfer media (see Thermodynamic Data Program, p. 108; Thermodynamic Properties of Zirconium Hydrides, p. 110). However, the mechanical, thermal, and chemical properties of high-temperature glasses, refractories, and other structural materials also receive emphasis (see

There is an urgent need for greatly accelerated work at high temperatures to provide reliable measurement techniques, standards, and basic data to aid in solving pressing problems. Important affected fields are missile and aircraft propulsion, atomic and thermonuclear energy, and aerodynamic heating. The Bureau's present capability for routine calibration of high-temperature devices is limited to about 3,000° C. It hopes to improve this capability by several thousand degrees in the next few years.

A. V. Astin, Director, NBS

more conventional temperature ranges. However, the new developments in science and technology have caused a continually increasing number of Bureau projects, covering a wide variety of fields, to be extended into the high-temperature range. Thus, the present high-temperature research program[1] has developed within a comparatively short time, mainly as a result of the Bureau's efforts to meet its assigned responsibility for the development of precise measurement methods and determination of the basic properties of materials.

This increase in high-temperature research, though important and valuable to the Nation, falls far short of meeting the current and future needs of American science and industry as they are presently visualized. However, a special effort is being made to utilize available facilities and staff in those investigations which are most urgently needed and which the Bureau is in the best position to undertake.

In general, the high-temperature research program may be divided into three broad areas of activity: (1) Studies of structure; (2) determination of properties and constants of materials; and (3) development of methods and instrumentation for high-temperature measurements.

Properties of Materials at High-Temperature, p. 112). In correlating and predicting the behavior of many high-temperature alloys and ceramics, phase equilibrium studies (pp. 119 and 120) are playing an important role.

A serious problem in high-temperature research has been the lack of adequate methods and instrumentation not only for producing and measuring high temperatures but also for determining changes in various kinds of materials at these temperatures. For example, special types of heat-resistant strain gages, giving reliable results under extreme conditions, are required for measuring mechanical properties. A number of techniques—such as differential thermal analysis, X-ray diffraction, and electric arc discharge—are now being investigated for use in determining high-temperature properties. Considerable work has also been done on furnaces for producing uniform high temperatures, and the temperatures of flames and other hot gases are being studied spectroscopically to provide methods of measuring temperature where conventional techniques cannot be applied. These and other activities in the field of high-temperature measurement will be treated in the July issue of this Bulletin.

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[1] *A bibliography of recent Bureau publications in the high-temperature field will appear in the next issue.*

Viscosity Measurements Above 2,000°C

A^S part of a program to develop techniques and instruments for measuring properties of materials at high temperatures, the Bureau's glass laboratory is developing an "oscillating-cup" viscometer to measure the viscosity of liquid inorganic oxides at temperatures up to 2,000° C or higher. The feasibility of the method for measurements in the anticipated viscosity range and
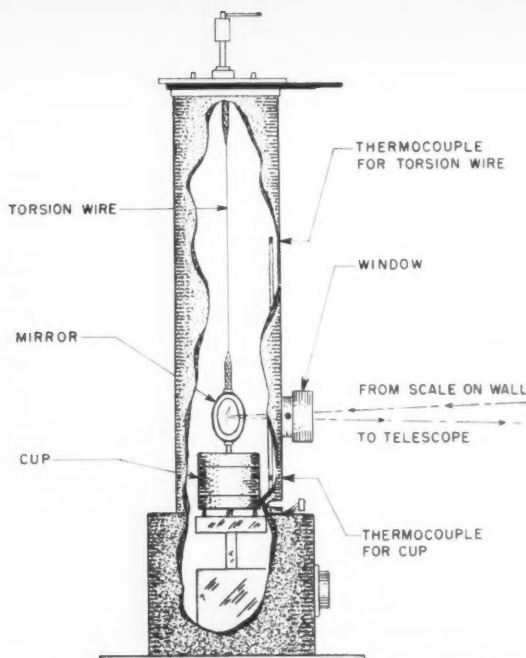

Prototype instrument for measuring viscosity of liquid inorganic oxides at temperatures up to 2,000° C and higher. This model was used to demonstrate feasibility of the method for the range of viscosities anticipated. Liquid is in closed cup suspended inside cylindrical housing (left) to form a torsion pendulum. Viscosity is determined from damping effect of liquid on torsional vibrations. Scientist follows vibrations by directing telescope to mirror attached to pendulum; mirror reflects scale on wall (not visible).

using convenient experimental cell (cup) dimensions has been demonstrated with a prototype model.

Values of the viscosity of a liquid and its rate of change with temperature find immediate application in fundamental research on molecular structure. Viscosity data are also of direct use in many technological problems—for example, in calculating forces required for the mechanical transport of a liquid.

However, before such data can be obtained for temperatures above 1,500° C, the array of problems that confront nearly all high-temperature measurements must be effectively met. Among the more serious difficulties are those of corrosion and vaporization at high temperatures. Both of these factors produce changes not only in the mass and geometry of the sample, but possibly in its composition as well; and stray vapors can react harmfully with critical parts of the apparatus. Also, for greater dimensional stability and reproducibility, it is desirable that the instrument be simple in shape and construction.

In the case of viscosity measurement, there is an additional specific requirement. At sufficiently high temperatures the viscosity becomes so small it can no longer be measured by the techniques in common use for liquids. The instrumentation must therefore be suitable for measuring low liquid viscosities well below the order of 1 cp (approximately that of water) for the inorganic oxides.

Oscillating-Cup Principle

The oscillating-cup method appears to be adaptable to the requirements mentioned. The principle of operation is simple. The sample liquid is enclosed in a cup that is suspended from a wire to form a torsion pendulum; and when torsional vibrations are started, the presence of the liquid causes them to be damped. As the amount of damping depends on the viscosity, the latter can be calculated from the observed rate at which the vibrations decay. The mathematical problem of deriving the viscosity from the rate of decay is rather complex, but an adequate approximate solution is available using a high-speed computer.

Decay of amplitude of vibration is exponential with time and only a few oscillations need to be observed to establish the decay rate. This increases the range of viscosities that can be measured in the relatively short times over which the high temperatures are easily maintainable. However, the method is primarily applicable for relatively low viscosities; higher viscosities would require inconvenient cup dimensions.

A prototype of an oscillating-cup apparatus has been constructed to investigate this method of measurement as applied to liquids. Measurements were made on oils having known viscosities in the range of interest and were carried out at room temperature and up to several hundred degrees C. The results show that the technique is satisfactory as a means of measuring low liquid viscosities. Parallel studies have also been made with a view to selecting materials and modifying the design to adapt it to use at high temperatures, and design of a high-temperature model is now well advanced.

High-Temperature Design

Studies of the corrosive effect of boron trioxide on molybdenum, tungsten, and tantalum at temperatures up to 2,100° C, have been made for the glass laboratory by Wright Air Development Center. These studies show that, of these metals, molybdenum offers the most resistance to corrosion, with the other two following in the order named. Initial plans call for a cup constructed of molybdenum plus 0.5 percent of titanium to counter-

Simplified cut-away drawing of prototype high-temperature viscometer. The three prongs fit into depressions in bottom of cup; turning knob (lower right) causes prongs to move cup to desired initial angular position. Electromagnet draws prongs downward to release cup and start vibrations. Controls at top are for centering and other mechanical adjustments of torsion pendulum.

is expected that this material will prove satisfactory for temperatures as high as a few hundred degrees above 2,000° C. For measurements at still higher temperatures it will probably be necessary to use other materials, possibly new types of ceramics now under development.

Chemical reactions within the cup will be further minimized by the gentleness of the motion between liquid and cup. Reaction products that do appear would tend to remain at the location where they are formed and to protect the regions separated by them from further reaction. The effect is analogous to the protection of some metal surfaces from extensive corrosion by the formation of a light metal-oxide coating.

High temperatures will be produced by induction heating and will be measured by optical pyrometry. Maintenance of a constant uniform temperature will be facilitated by the relatively small size of the oscillating cup as compared with the measurement cells of familiar types of liquid viscometers.

The cup will be affixed to a rigid rod which will extend outside the high-temperature zone, so that all moving parts of the apparatus except the cup can be maintained at lower temperatures where their operation is much more convenient. The rod is to be suspended from a torsion wire on which the rod and measurement cup oscillate as a unit. Measurement of the vibration amplitude will be made with a telescope directed towards a mirror attached near the top of the rod.

In addition to the work on the oscillating-cup viscometer, it is planned to explore the possibility of determining viscosity at high temperatures from measurements on the damping of ultrasonic oscillations of a small probe immersed in the experimental liquid. An attempt will first be made to modify commercially available probes to high-temperature use. The glass laboratory is also planning a survey of general techniques and specific designs for the measurement of surface tension at high temperatures, with the aim of selecting one or more for intensive development effort.

act embrittlement encountered with pure molybdenum at high temperatures. The cup will be protected from oxidation by operating it in a vacuum or in an inert atmosphere such as nitrogen or argon made slightly reducing by addition of a few percent of hydrogen. It

High-Temperature Transformations

IN the high-temperature research program of the Bureau, attention is given not only to measurement of properties of materials at elevated temperatures, but also to the way in which materials are transformed and their properties change as the temperature rises. Interest centers on the rates at which various properties change, temperature ranges in which special phenomena occur, sudden transitions that take place at fixed temperatures, and changes induced by combining high temperature with high pressure. The usefulness of a material for high-temperature applications is largely determined by the nature and extent of such changes.
As a solid is heated it expands, and the expansion may continue smoothly up to the melting point. However, for certain solids the volume may change abruptly at some fixed temperature even well below the melting point; this signals a major structural change, called an

inversion, caused by rearrangement of the atoms into a different crystal pattern. As heating continues, the atomic arrangement may change to allow a certain amount of freedom in the interatomic bonding, so that the solid begins to flow or creep, with important consequences for the engineering properties of the material.

At a definite temperature, transformation from solid to liquid occurs—that is, the solid melts. Interest then shifts to such properties as viscosity and surface tension and their rates of change with temperature. In some cases, if the temperature of the liquid is suddenly and substantially reduced, the material solidifies in the noncrystalline, vitreous state. The constitution of such quenched or frozen liquid-glass is a subject of special study.

The transition from solid or liquid to gas is another change of prime importance at high temperatures; the
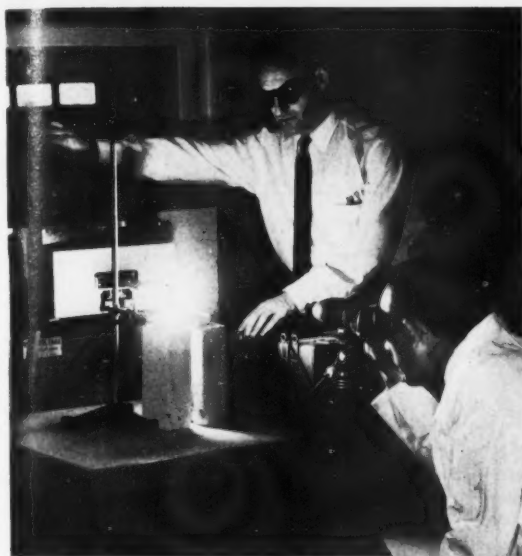
Observing the melting behavior of a ceramic. Sample in crucible is inside glowing graphite susceptor that is heated by the induction coil around it. Sample, visible through a small hole, is observed by scientist with optical pyrometer (foreground).

this variation has been attributed to heat treatment—the higher the temperature of preparation, the higher the inversion temperature.

This inversion has been reinvestigated by the Bureau, using specially purified material. The results show that inversion occurs at a fixed temperature (271° C) provided that the cristobalite has been prepared at a sufficiently high temperature (above 1,400° C) to effect proper crystal perfection.[1]

Several other refractory oxides that show solid-phase inversion have also been studied. One of the more interesting is zirconium oxide. At low temperatures the crystallographic form of zirconium oxide is monoclinic, but above 1,000° C it inverts to a tetragonal form which is stable up to the melting point. However, the addition of a small amount of calcium oxide to the zirconium
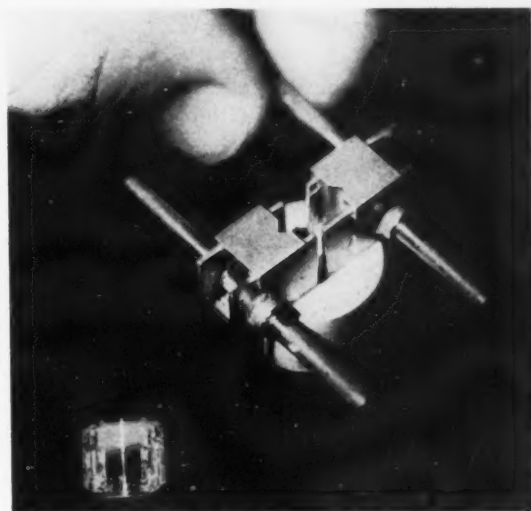
Diamond (front left) used as a high-pressure cell. Sample of material to be studied is placed in narrow hole bored through diamond and compressed between steel pistons (front right). Changes in sample are detected by studying the way it transmits infrared light. Mount (center) for diamond has 4 "curtains" to limit the infrared beam; position of each curtain is adjusted (as shown) by turning projecting rod.

rates at which such changes occur determine the stability of the material to erosion and evaporation. The effects of other gases in the environment, which often have considerable influence on the evaporation process, must also be studied.

Superimposed on all the transformations mentioned are the effects of impurities, whether present in large or only trace amounts.

Finally, the role of an increase in pressure must be considered. Its effect on the properties of solids is usually opposite to that of an increase in temperature. Study of the interplay of these two factors has proved one of the more interesting areas of modern high-temperature physics and chemistry.

Research at the Bureau is concerned with each of these various changes in the behavior of materials as they are heated. In the following, brief descriptions are given of work being done on some of them.

Inversion

Inversion studies are of interest because they contribute to our knowledge of the volume stability of materials in various temperature ranges. At the Bureau such studies have been made on refractory oxides, including the technologically important substance, silicon dioxide. This compound has several forms, including quartz and cristobalite. Quartz is a low-temperature form, while cristobalite can exist in two modifications that are stable at low and high temperatures, respectively. The temperature at which inversion from high- to low-temperature cristobalite occurs has been reported at different values from 180° to 270° C. In the past

oxide stabilizes another (cubic) form; this form persists from melting point down to room temperature without inversion, and therefore without the undesirable volume change that accompanies inversion. Zirconium oxide is thus converted to a useful, volume-stable refractory.

Creep and Crystal Defects

Plastic deformation (creep) and ultimate strength are among the physical properties of solids that depend strongly on the presence of lattice defects and impurities. The Bureau is investigating such processes in

metallic oxides; and among these, aluminum oxide was chosen for concentrated study because it is one of the strongest of the refractory materials and is available both as large single crystals and in polycrystalline form.

It was found [2] that single-crystal aluminum oxide begins to exhibit creep at 900° C; at 1,000° C some of the crystals could be stretched by 2 percent. This extension always results from the same type of motion relative to the crystal structure—that is, by slip along the hexagonal base plane in the direction of an "a" axis; so that plasticity at 1,000° C is an extremely anisotropic property. For extension to occur, the tensile stress must be applied obliquely to the base plane; if the stress is either parallel or perpendicular to the base plane no creep appears until the temperature is increased to 1,600° C, when some other unidentified mode of deformation becomes active. However, at 1,500° C a crystal subject to a tensile stress at an
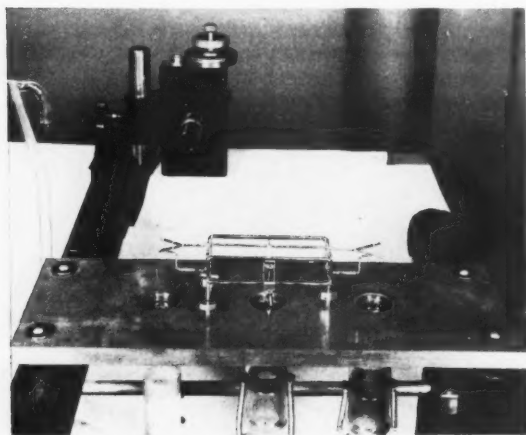
Microbalance used in studies of vaporization and sub-limitation at high temperatures. Specimen is suspended from left arm (foreground) into furnace (not visible); counterweight is suspended from balance arm at right. Deflection of balance as material is lost through sublimation is observed with cathetometer telescope (rear).

angle of 45° to the hexagonal base plane can be extended to more than twice its original length.

The deformation occurring in these crystals has two characteristic features. First, it requires an incubation period at 1,000° C for as long as 70 hr under stress before measurable creep occurs. If the specimen is then held at the same temperature and under constant stress, there is first a period of increasing creep rate after which the rate decreases, approaching a constant value. At higher temperatures the incubation period is shorter or absent altogether, and a final period of accelerated creep (associated with "necking" of the crystal) may occur.

Second, at a given temperature, a certain value of stress—the creep yield stress—must be exceeded to

initiate measurable creep; this value of the stress is strongly temperature-dependent. At 1,400° C a tensile stress of 250 kg/cm² is sufficient to initiate creep; at 900° C, 1,560 kg/cm² is required; and at lower temperatures the specimens always failed in a brittle manner without measurable plastic deformation. Further experiments showed that once creep had started at 1,000° C, it would continue at a stress considerably below the creep-yield stress.

The presence of impurities can raise the stress required to start creep; at 1,200° C specimens with less than 1 percent of chromium oxide had a creep-yield stress about twice as large as that for pure aluminum oxide. These results call for interpretation in terms of the stress necessary to move dislocations in the aluminum oxide structure.

Polycrystalline aluminum oxide [3] behaved in a completely brittle manner at room temperature. However, at 1,000° C it exhibited a type of plastic deformation quite different from that found in single crystals. Small amounts of creep took place at stresses well below the creep-yield stress for single crystals; the creep began immediately on application of load and the creep rate steadily decreased thereafter. When the load was removed after 10 hr, as much as half the total deformation was recovered by creep in the opposite direction in the following 10 hr. The mechanism of this creep and subsequent recovery is thought to be grain-boundary slip.

Creep in aluminum oxide and in other refractory metal oxides that have been studied in less detail depends on two types of defects—dislocations and grain boundaries—and on their interaction with impurities. Dynamic measurement of elastic moduli and internal friction provide a sensitive means for studying defects and impurities; a method has been developed for making such measurements at temperatures above 1,000° C. Experiments are now underway to study the effects of grain-boundary viscosity and dislocation motion on the temperature, frequency, and time-dependence of Young's modulus and the internal friction.

Vaporization and Sublimation

Advanced research on rockets and nuclear power plants has emphasized the inadequacy of present knowledge regarding vaporization or sublimation processes at high temperatures. The lack of knowledge results in part from the view—held not too long ago—that the vapor phase plays no important role in the high-temperature processing or technological application of solids. However, a growing body of evidence suggests that while sublimation processes may not in general be rate-determining, they often have a major influence on reactions at high temperatures.

In line with the changed outlook, it is no longer common to assume that metals vaporize as monomers, or that ionic compounds retain in the vapor phase the valency relations characteristic of the solid phase. High-temperature chemical studies have, in many cases, revealed a complete reversal of low-temperature be-

havior; so that the experimenter is faced with the possible existence of a large number of molecular species quite beyond his usual experience.
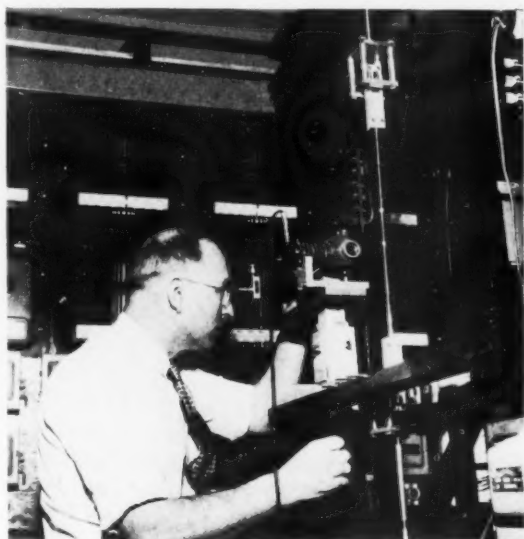
Four main aspects of high-temperature vapor phenomena are of current interest. These may be termed the kinetic, microscopic, thermodynamic, and chemical aspects, and are concerned, respectively, with: (1) The quantity of material that vaporizes from unit area in unit time, or the rate of linear regression of a surface in a vacuum or in contact with various gases; (2) the mechanism by which individual atoms or ions acquire sufficient energy to leave the surface; (3) the energies associated with phase changes and reaction; and (4) identification of the vaporizing species and the reactions occurring at the interface between solid or liquid and gas phases.

These aspects are not entirely independent. Thus, if kinetic data on loss of weight in a vacuum is combined with data on molecular weights of the vaporizing species, one can calculate the equilibrium vapor pressure and the heat of vaporization. Or, knowing the elements involved and the order of magnitude of the thermodynamic functions, a reasonable estimate can be made of the vaporizing species present.
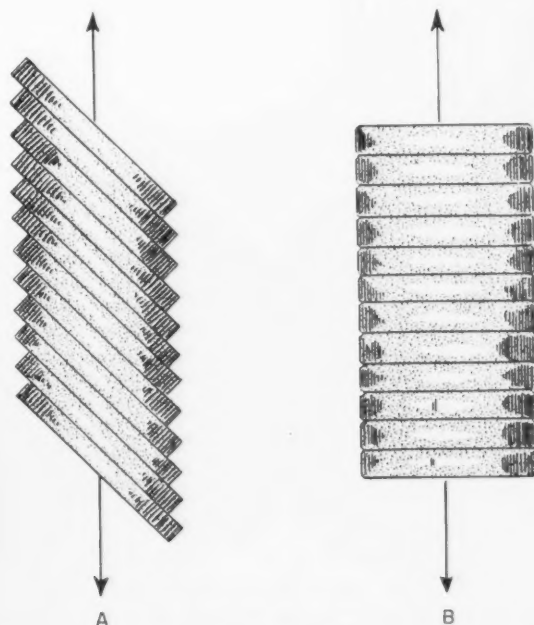
Recently the Bureau has been measuring the loss in weight at high temperature of single and polycrystalline specimens of known surface area. Changes in weight are measured with a Gulbransen-type microbalance designed for loads up to 4 g and with a sensitivity of 1 μg. Specimens are suspended from the balance and, if they are electrically conducting, are heated by direct

induction. If nonconducting, they are suspended in an inductively heated furnace; i. e., the specimen is held near a "susceptor", or material capable of being heated inductively. Choice of material and design for the susceptor present severe problems, since the susceptor can interfere with the free escape of molecules from the specimen and can also react harmfully with both the specimen and surrounding gases.

This problem is also being approached with the help of a solar furnace, and various other measuring techniques are being used. Both the Knudsen technique and transpiration methods find application in the problems under study, and it is planned eventually to use mass-spectrometric methods to establish the molecular weights of the vaporizing species. Studies are now being made of the different measurement techniques to determine the relative merits of each.

Diagrammatic models of the mechanism of creep in aluminum oxide single crystals at 900° to 1,600° C. Disks (seen edgewise) represent layers of atoms parallel to the hexagonal base plane. A: Tension is applied obliquely to base plane and disks slip past one another, causing crystal to elongate. B: Tension perpendicular to the base plane, and no stretching occurs. Stretching is also absent when tension is parallel to base plane.

Measuring the elongation of a sapphire (aluminum oxide) crystal in study of creep at high temperatures. Crystal, in form of rod (right) is subjected to vertical tension; elongation of portion betwen cement bands (small spheres) is measured with optical extensiometer. Cylindrical electric furnace with window has been removed so crystal may be seen.

As an example of the results obtained thus far, it has been possible to show that water vapor has no measurable effect on the rate of evaporation of alumina up to 1,600° C. but that at the melting point (2,050° C) it considerably enhances the rate of evaporation. Furthermore, by increasing the partial pressure of oxygen in the surrounding region, the rate of evaporation can be retarded.

High Temperature Plus High Pressure

It is well known that greater pressure favors the formation of compounds with higher density; so that, for example, the pressures existing far below the earth's surface are largely responsible for the formation of gems and other high-density substances with unusual properties. An investigation now underway aims to imitate this natural process and, by a simultaneous application of high temperature and high pressure, to synthesize crystals of high purity and to measure precisely their properties.

Thus a form of talc has been produced in which part of the water is replaced by fluorine; this new form has proved stable, that is, it persists after the pressure and temperature are returned to normal. Similar experiments with water and with lime, on the other hand, generated crystalline forms that continued only as long as the extreme conditions were maintained. Also, the plastic, polytetrafluorethylene, was found to take several new but temporary forms. In another experiment, the gem beryl ($3BeO \cdot Al_2O_3 \cdot 6SiO_2$) was synthesized and its stability limits, as well as those of natural beryl, were determined.

An unusual piece of apparatus used in this work is a 7.5-carat diamond, confiscated from a smuggler by the Bureau of Customs and turned over to the National Bureau of Standards by the General Services Administration. The diamond is a flawless specimen of the rare type II that is transparent to infrared radiation up to wavelengths of 20 μ. This has the advantage that, when the diamond is used as a pressure cell, it is possible to obtain the infrared transmission spectrum of the material being studied; and this, in turn, yields important information about changes taking place in the arrangement of the atoms within the material.

The original emerald-cut diamond was modified into a pressure cell by drilling a hole 0.015 in. in diameter through its center. Two pistons of hard tool steel that closely fit the hole are inserted, one from each end, with the sample under study between them. Because of the small cross section of the cell, a force of only 80 lb is required to bring the internal pressure to 450,000 psi (the maximum that can be attained without danger of splitting the diamond).

Among the other equipment for such studies are steel bombs fitted with opposing pistons of special alloys. External force is applied by hydraulic press and internal pressures as high as 1 million psi and temperatures up to 1,500° C are obtained. Alterations of the specimens within the pressure chambers are followed by measuring the changes in volume and electrical properties; in some experiments more indirect methods must be used.

[1] The inversion temperature of cristabolite, by R. F. Walker, S. Zerfoss, S. F. Holley, and L. J. Marston, J. Am. Ceram. Soc. (in press).

[2] Plastic deformation of ceramic-oxide single crystals II, by J. B. Wachtman Jr. and L. H. Maxwell, J. Am. Ceram. Soc. 40, 377 (1957).

[3] Creep of crystalline nonmetals, by J. B. Wachtman Jr., paper published in book, Creep and Recovery, Am. Soc. Metals (1957).

Property	Units	Temperature in °K									
		2750	3000	3250	3500	3750	4000	4250	4500	4750	5000
ΔH°	kcal/mole	-29.98	-30.56	-31.14	-31.74	-32.37	-33.04				
ΔF°	kcal/mole	-19.77	-25.10	-23.00	-21.32	-16.76	-24.11				
$log_{10} Kf$		6.6873	5.4180	6.2437	5.8724	5.5834	5.8412				
$(F^\circ - H_0^\circ)/T$	cal/deg mole	-56.608	-57.324	-57.000	-58.578	-59.150	-59.608	-60.195	-60.676	-61.132	-61.588
$(H^\circ - H_0^\circ)/T$	cal/deg mole	8.0782	8.1448	8.2040	8.2572	8.3051	8.3487	8.3885	8.4252	8.4588	8.4905
S°	cal/deg mole	64.086	65.459	66.172	66.835	67.455	68.037	68.585	69.101	69.581	70.056
$H^\circ - H_0^\circ$	cal/mole	32215.	34434.	36660.	38900.	41144.	33395.	35651.	37913.	40180.	42452.
C_p°	cal/deg mole	8.886	8.680	8.937	8.985	8.990	9.015	9.038	9.058	9.078	9.096

Table title: CO (g) — HEAT, FREE ENERGY, AND EQUILIBRIUM CONSTANT OF FORMATION, FREE ENERGY FUNCTION, HEAT CONTENT FUNCTION, ENTROPY, HEAT CONTENT (OR ENTHALPY), AND HEAT CAPACITY. Reference States for Elements, Used for Calculating ΔH°, ΔF°, and $log Kf$: C (c, graphite); O_2 (g)

THE BUREAU, in a program supported in part by the Atomic Energy Commission, is collecting and compiling data on the chemical thermodynamic properties of a great number of materials. The object of the program is to present, in convenient tabular form, a critical summary of the thermodynamic information available on each chemical substance over as wide a temperature range as possible.

The development of high-energy fuels and nuclear power sources has brought into sharp focus the need for thermodynamic data, particularly at high temperatures and pressures. Experimentation in these fields is difficult and costly; it requires a knowledge of energy yields from which reactions will proceed, and the stability of materials under various temperatures and pressures. Thus, predictions and calculations based on the classical methods of chemical thermodynamics are playing an increasingly important role in guiding the engineer working on these developments. However, such predictions can be made with accuracy only when

the thermodynamic properties of all the chemical species participating in the actual system are available.

The tables compiled by the Bureau contain values of heat-content function, free-energy function, entropy, heat capacity, and heat and free energy of formation. For each substance the values are given at regular intervals of temperature from 0° to as high as 6,000° K in some instances. From these data, answers may be obtained to many questions regarding stability, equilibrium compositions, and energy yields in this temperature range.

Many types of scientific research provide data for the chemical thermodynamic tables. Valuable sources of information include not only experimental calorimetry, thermochemistry, and thermodynamics, but also such diverse fields as X-ray and electron diffraction, atomic and molecular spectroscopy, and mass spectroscopy. Laboratories in countries all over the world are exploring these areas of measurement, and experimental results are published in a variety of technical periodicals. However, to obtain useful thermodynamic information from these results, they must first be assembled, correlated, and then fitted together into a self-consistent whole.

To compile tables for a particular substance, the values of at least one heat of reaction at a known temperature must be ascertained, as well as the values of heat content and entropy as a function of temperature up to the highest temperature of interest. Heats of reaction are generally obtained from published experimental calorimetric measurements. But when the desired reaction is not susceptible to direct measurement, these heats are computed in the Bureau's thermochemistry laboratory from a related set of measurements.

In making these computations, special precaution must be observed in selecting auxiliary data so that a final self-consistency is assured in the tabulated values. Hence, all values used are carefully analyzed with respect to the units of measurement employed, temperature scale, and calibration methods. When calorimetric data are not available, as is often the case, the necessary heats of reaction are obtained from measurements of equilibria and their temperature dependence, from spectroscopic and other molecular techniques, or by correlating energy content with temperature and molecular structure.

The thermodynamic functions of molecules, which are necessary to convert heat data to equilibria at different temperatures, may be obtained from experimental measurements of heat capacities and heat contents for solid and liquid phase materials. For many gaseous molecules, however, more accurate values of the functions are derived by statistical calculation rather than by calorimetric measurement. This method requires a knowledge of both the molecular structure and the characteristic vibration frequencies of the substance. Also necessary is a knowledge of the molecular geometry. This is obtained from X-ray or electron diffraction measurements or from microwave absorption spectroscopy, followed by a detailed analysis of the infrared and Raman absorption spectra of the substance.

In order that the tables may make full use of available information, the Bureau maintains a current record of all pertinent data. The most significant categories are: (1) Experimental heats of reaction, fusion, and vaporization; (2) vapor pressures; (3) solubilities; (4) electrochemical cell measurements; (5) heat capacities; (6) experimental and statistically calculated entropies; and (7) molecular and spectroscopic data. Abstracts of the original data are indexed according to chemical composition of the substance studied. After all of the known data relating to the properties of any one substance are assembled, the data are analyzed and the current "best" values selected for the various thermodynamic properties.

These values are tabulated and distributed in looseleaf form without charge to Government, university, and industrial research laboratories having need of the service. In addition, detailed reports covering certain special classes of compounds are periodically made available.[1] A general summary of experimental calorimetric data covering heats and free energies of formation at room temperature is presently being prepared. When published, the summary will constitute a revision to a current Bureau compilation of selected values of chemical thermodynamic properties.[2]
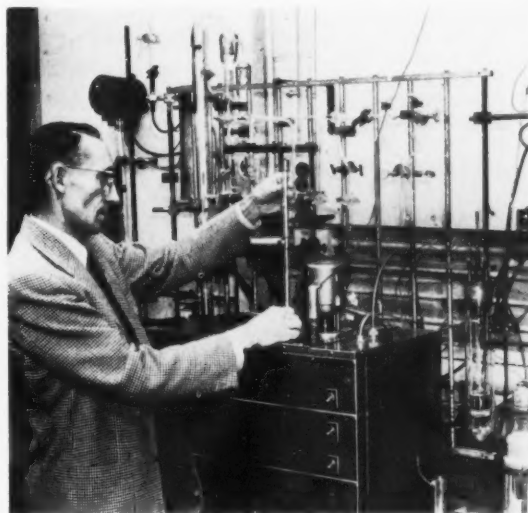
Apparatus used to measure heats of formation and decomposition at high temperature in the thermochemistry laboratory.

[1] Thermodynamics of some simple sulfur containing molecules, by W. H. Evans and D. D. Wagman, J. Research NBS **49**, 141 (1952) RP2350; Thermodynamic properties of the alkali metals, by W. J. Evans, R. Jacobson, T. R. Munson, and D. D. Wagman; **55**, 83 (1955) RP2608; Thermodynamic properties of some gaseous halogen compounds, by W. H. Evans, T. R. Munson, and D. D. Wagman; **55**, 147 (1955) RP2614.
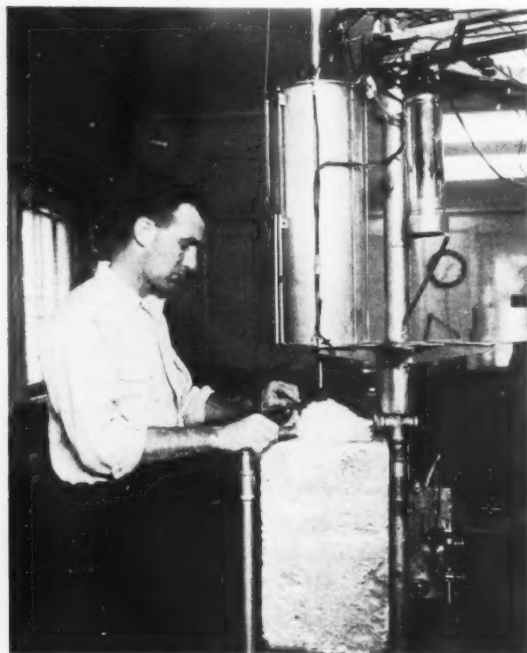
[2] See Selected values of chemical thermodynamic properties, NBS Circ. 500 (February 1952) Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. ($8.25).

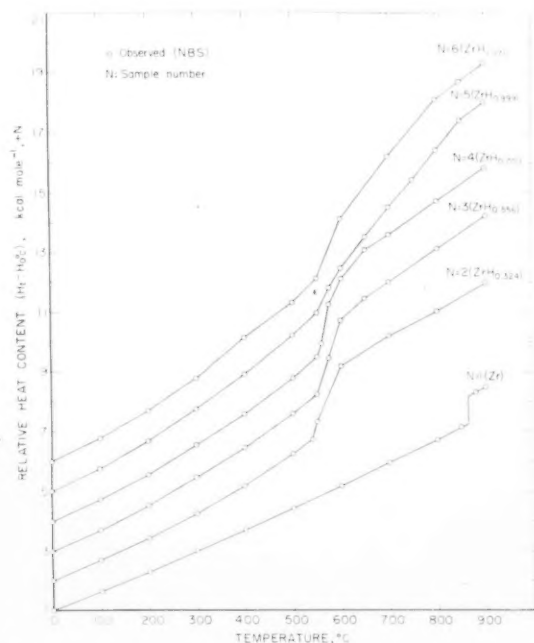# Thermodynamic Properties of Zirconium Hydrides

THE BUREAU has been conducting research on specific heats in cooperation with the Materials Laboratory, Wright Air Development Center. In the course of this work, T. B. Douglas of the thermodynamics section of the Heat Division has developed accurate methods for determining some of the more important thermodynamic properties of the zirconium-hydrogen system from specific heat data. These methods, which can be conveniently applied to many other heterogeneous systems, are expected to be of value in predicting the high-temperature behavior of a wide variety of materials. They should be particularly useful in determining the properties of systems in which heat exchanges due to chemical reactions between the constituents occur over the temperature range under study.

The hydrides formed when zirconium absorbs large quantities of hydrogen are solid, alloy-like substances, stable to remarkably high temperatures. Together with the hydrides of other transition metals—such as titanium and uranium—they form a unique class of materials whose properties often differ markedly from those of other substances. In recent years there has been an intensified effort to investigate these properties more completely and systematically because of their importance in metallurgical and other problems. For example, the embrittlement of slowly cooled zirconium metal has been shown to be due to the reaction of traces of hydrogen with the metal to form an insoluble hydride phase. Complete data on the thermodynamic properties of the zirconium hydrides would not only permit a more reliable prediction of their chemical behavior at high temperatures but would also make possible a

Heat-content data plotted against temperature for several compositions of the zirconium-hydrogen system. All five of the zirconium hydrides show rapid rises of heat content with temperature between 550° and 600° C, corresponding to the appearance of the beta phase.

clearer theoretical understanding of the forces which determine their structures and properties.

The methods used in the present investigation of thermodynamic properties require highly accurate determination of the specific heats of the samples over the temperature range involved. Data were obtained to the desired accuracy with apparatus developed and refined over a period of years for use in making precise measurements on specific heat standards.[1]

The specific heats from 0° to 900° C of zirconium metal and of five samples of zirconium hydride (containing from 0.35 to 1.17 percent hydrogen by weight) were measured [2] precisely in an ice calorimeter by the "drop" method. In this method the sample, sealed in a container, is suspended in the furnace until it comes

Apparatus used to obtain accurate specific heat values for zirconium hydrides. The sample material is first heated to a known temperature in the cylindrical resistance furnace (above) and is then dropped through the tube into the ice calorimeter (enclosed in insulation, below).

to a known constant temperature. It is then dropped into the calorimeter where it melts ice in equilibrium with water in a closed system. The resulting volume decrease in the ice draws mercury into the system, and the mass of mercury moved is proportional to the heat energy lost by the sample (relative heat content) in cooling from its initial temperature to 0° C.

The data obtained in this way were then applied to evaluate the limits of composition of the various phases of the zirconium-hydrogen system at temperatures between 0° and 900° C. Two methods, each based on older techniques, were developed. One method takes advantage of the fact that the energy-composition isotherms show breaks at any phase-diagram boundary separating two phase fields. These breaks in the isotherms can be determined from the sudden increase in specific heat when the sample reaches a temperature where a new phase appears. Thus, the method is actually a refinement of the cooling curve method for obtaining phase compositions. However, it can be used with many all-solid systems that approach equilibrium quite slowly. Here the cooling curve method would be impractical.

The second method determines the limits of phase composition by locating the compositions where the pressure isotherms derived from the specific heat data show breaks. Results agreeing with the first method and with older methods were obtained when it was assumed that the pressure isotherms have shapes which support an earlier conclusion. This conclusion was that when zirconium metal dissolves hydrogen gas, the hydrogen molecules are broken up into atoms to form true hydrides.

The experimentally obtained specific heats were also used to obtain a measure of the relative energies of the various hydride phases at different temperatures. Whenever a temperature is reached where a new phase appears, the increase in specific heat can be attributed quantitatively to the energy of creating the new phase from the old. Based on this principle, a method was developed which made it possible to calculate the heats of formation of a great number of zirconium hydrides over the whole temperature range, using a single previously known value for one of the hydrides.

Considerable information was obtained regarding the beta zirconium hydrides, which are unstable at lower temperatures and thus cannot be studied readily by room-temperature techniques; at high temperatures their crystal structure is the same as that of zirconium metal. A marked absorption of heat was observed at the eutectoid temperature. This was due to the formation of the beta solution of zirconium and hydrogen from the lower-temperature hydride structures, with the absorption of 2.2 kcal/mole. These solid beta solutions are analogous to liquid solutions so commonly encountered above their eutectic temperatures, and the unusually high entropies of the beta solutions reflect the liquid-like disorder of the hydrogen atoms in the interstices of the crystalline zirconium lattice. Neutron diffraction data show that when enough hydrogen is added to the beta solutions to approach the composition ZrH_2, a tetragonal lattice is formed. Each unit cell of this lattice has four faces on which hydrogen atoms can be located. No corresponding diffraction data are available to locate the hydrogen in the beta phases, but it is known that the unit cell is cubic
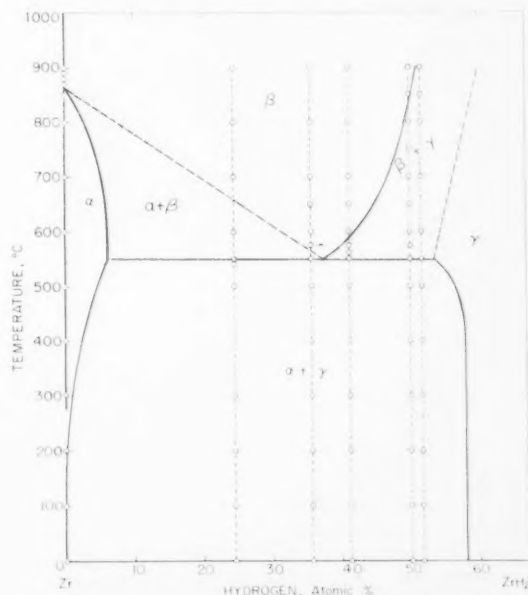
Phase diagram of the zirconium-hydrogen system. The dotted vertical lines indicate the compositions experimentally measured in the present investigation and the points for each sample show the temperatures at which its relative heat content was established.

instead of tetragonal and thus would provide six equivalent faces on which hydrogen atoms could be located. This concept is supported by the high entropies obtained for these phases. These entropies show, in fact, that the beta phases contain at least 50 percent more hydrogen sites than do the more ordered tetragonal lattices.

[1] An improved ice calorimeter—the determination of its calibration factor and the density of ice at 0° C, by *Defoe C. Ginnings* and *Robert J. Corruccini, J. Research NBS* **38**, 583 (1947) RP1796. See also Improved ice calorimeter in high-temperature research, *NBS Tech. News Bul.* **31**, 63 (1947).

[2] The heat content of zirconium and of five compositions of zirconium hydride from 0° to 900° C, by *Thomas B. Douglas* and *Andrew C. Victor, J. Research NBS* (to be published).

Scientist testing an experimental ceramic coating that has been placed on the heat exchanger of an aircraft engine to enable the metal to withstand high-operating temperatures.

THE OBJECTIVE of the Bureau's program in inorganic materials is to provide an integrated body of data on their basic properties from which useful information on large classes of substances may be obtained for specific application. The program includes a study of the factors governing the behavior of glasses, enamels, refractories, gases, metals, and alloys at high temperatures. Current research includes the measurement of chemical reaction rates, calculation of thermodynamic quantities, synthesis of pure inorganic crystalline compounds, determination of mechanical properties of solids, and measurement of high-temperature radiation characteristics, which would lead to the development of new and improved high-temperature-resistant materials.

Thermodynamic Properties of Gases

The quantitative relations between the heat in a gas and the work done by the gas as it expands are important in describing how the gas acts at high temperatures under the extreme conditions encountered, for example, in rocket power plants. An important characteristic of gases in such high-temperature applications is the relative ease with which heat flows through the gases when a temperature difference exists. Since highly energetic flow of gas is rarely of a simple, smooth nature, the ordinary thermal-conductivity measurement technique is not sufficient for heat-flow determinations. Information must be obtained on other quantities such as viscosity, and, in the common case of a chemically reacting gas mixture, on rates of material flow due to diffusion.

The Bureau has been able to estimate these transport properties and also the thermodynamic properties for common gases up to quite high temperatures. Because these temperatures extend far above the regions of accurate direct measurement, it has been necessary to compute properties according to fundamental principles of statistical mechanics, using the information available on energies of the internal quantized states for the various constituents. From this information, empirical estimates can be made concerning the way in which interaction energies between individual molecules, free radicals, atoms, and ions depend on their instantaneous positions in space relative to each other. When experimental data relevant to related properties at lower temperatures are available, comparison may in some cases supply part of the necessary data upon which estimates of high-temperature properties can be based.

Various aspects of the work on the properties of air have indirect application to estimates of its properties at high temperatures. Measurements below ordinary room temperature include liquid-vapor phase equilibria for oxygen and nitrogen mixtures, heats of vaporization and surface tension for oxygen and nitrogen and their mixtures, and simultaneous measurements of pressure, specific volume, and temperature for air from room temperature down to 125° K shortly to be extended upward toward 1,000° K. Using tabulated values for the constituents of air based on spectroscopic data available, the thermodynamic properties of air have been calculated in the region from 10^4 degrees to 5×10^6 degrees K, omitting molecular formation, for densities from ten times normal down to 10^{-6} normal. For the more limited region up to 15,000° K, thermodynamic calculations on the formation of molecules have also been made for argon-free air from 100 times normal density down to 10^{-6} normal density.

Chemical Reactions

Although a considerable body of experimental and theoretical knowledge has been accumulated about

High Temperatures

liquid and gas phase reactions at temperatures up to a few hundred degrees, at higher temperatures this field remains largely unexplored. Many such reactions, particularly those between a solid and its gaseous environment (for example, a metal and atmospheric oxygen or nitrogen), involve a change in mass. The rate of such reactions can thus be conveniently determined on small-scale specimens by following the change in weight of the specimen during the reaction.

To study such reactions, the Bureau has constructed a quartz microbalance operating inside a glass vacuum envelope, together with associated heating and vacuum equipment. The balance can measure weight changes of the order of 0.2 to 0.3 μg. On a specimen having a surface area of 5 cm^2, this would correspond to about one layer of oxygen molecules. The instrument can aid in studying reaction rates at temperatures up to about 1,400° C at gas pressures ranging from atmospheric down to 10^{-6} mm. It has been designed to determine gas absorption and the vaporization behavior of solids at elevated temperatures.

The microbalance is being used to study the oxidation behavior of metallic niobium (columbium), a material that oxidizes rather rapidly at temperatures higher than 200° to 300° C. Its oxidation rate is subject to a number of complexities which make it of theoretical interest. If its tendency towards rapid oxidation could be overcome, it would be of considerable practical interest as a high-temperature structural material because of its high melting point, ease of fabrication at room temperatures, and low-neutron capture cross section.

Synthesis of Crystalline Compounds

Closely related to this work is the synthesis of pure inorganic crystalline compounds that can be used to measure precise constants. Most natural compounds or minerals contain varying amount of impurities which alter their true properties; however, little is known concerning how these properties change with a given impurity. One of the program objectives is to add controlled amounts of impurities to the synthetic compound and to measure the change in properties as compared to the pure analog.

Synthesis or crystallization experiments are carried out at high temperatures and pressures using the techniques of solid-state reactions, hydrothermal reactions, and reactions obtained from a crystallizing melt. In a

steel bomb with a hollow center, temperatures up to 1,500° C and pressures up to 10,000 atm may be reached. Pressure is generated by pumping inert gas into the reaction chamber; the high temperatures are obtained by means of an internal electrical resistance element of platinum or tungsten. The apparatus can also be used to study differential-thermal reactions at elevated pressures. Another apparatus that can attain temperatures up to 1,000° C and pressures up to 50,000 atm consists essentially of two opposing tungsten carbide cyclinders of $1/4$-in. diameter, surrounded by an induction heating coil. The material to be reacted is placed between the two pistons. In this case pressure is obtained from a hydraulic press.

Studies are now in progress on the conditions necessary to synthesize such pure silicates as: (1) Beryl or emerald ($2BeO \cdot Al_2O_3 \cdot 6SiO_2$); (2) the humites ($n$ $Mg_2 \cdot SiO_4 \cdot MgF_2$), where $n = 1$, 2, 3, and 4; or (3) coesite (SiO_2), a new dense polymorph of quartz. Beryl, which melts incongruently at a temperature of 1,425° C at 1 atm of pressure, can be synthesized hydrothermally or from solid-state reactions at temperatures of 850° C and pressures of 20,000 psi, using formula proportions of the constituent oxides or sulfates. All the reactions take place in sealed platinum containers. Attempts are now in progress to substitute ions in the beryl structure which are known to substitute for

High-temperature creep testing of stainless steel specimens. Under evaluation are the effects of variations in heat treatments on the mechanical properties of stainless steels.

similar ions in other structures. For example, it is known that germanium will substitute for silicon in structures such as forsterite (Mg_2SiO_4). It is possible that germanium will substitute for silicon in beryl. If this reaction can be carried out, the properties of the resulting germanium beryl should be quite different from those of the silicon beryl.

The humites have been synthesized under variable conditions of high temperature and pressure, and recently a complete substitution of germanium for silicon was achieved in the structure having the composition of $Mg_2GeO_4 \cdot MgF_2$. The optical properties and the density of the material were found to be increased by the substitution.

Coesite, a dense polymorph of SiO_2, can be synthesized at 700° C and 30,000 atm. Infrared transmission techniques have demonstrated that its structural framework (SiO_4 tetrahedra) is the same as that of quartz. The difference in density between quartz and coesite is due primarily to a rearrangement of the SiO_4 tetrahedra and not to any distortion of the individual tetrahedra.
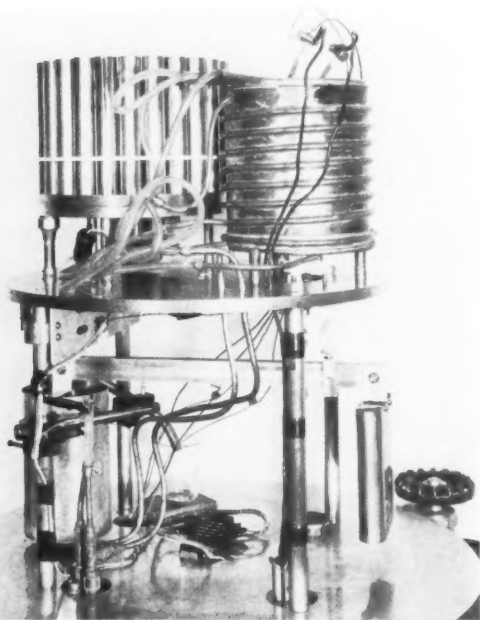
Apparatus to measure the flexural strength of uranium dioxide and thorium dioxide specimens at temperatures up to 1,000° C.

Mechanical Properties of Glasses

Engineering data on a number of representative glasses near the upper limits of their potentially useful temperature range are being obtained with the support of the Wright Air Development Center and the cooperation of several of the commercial glass producers. The properties under study are the strength, or modulus of rupture; the modulus of elasticity; Poisson's ratio; stress-rupture, or static fatigue; and creep. The test temperatures range from room temperature to near the strain point of the glass, with 940° C being the highest temperature at present. Glass is tested with both short- and long-term exposures up to 500 hr.

The strength of glass is greatly affected by surface conditions, internal strain (including the intentionally introduced strains in "tempered" glass), rate of loading, and humidity of the atmosphere. These conditions are systematically varied with the testing temperature and with the heat treatment before testing.

Reliable strength measurements are difficult to obtain on glass even with closely controlled sample preparation and testing conditions. It was found, however, that controlled abrasion of the surface of the samples gave more uniform, but lower results than were obtained with polished samples. However, the strengths of the weakest samples of each group appeared to be approximately the same. Statistical treatment of the test results has aided in evaluating the effect of the various conditions on strength and in the planning of future tests.

Protective Coatings for Metals and Alloys

Practically all metals and alloys of practical interest oxidize when heated to high temperature. This oxidation weakens the material and, in some cases, completely prevents the use of certain high-strength metals and alloys for such high-temperature applications as gas turbines and nuclear reactors.

The Bureau has been actively engaged in finding ways of reducing this corrosion at high temperatures. One approach is a ceramic coating. Such coatings are normally applied at a thickness of 0.001 to 0.002 in. and
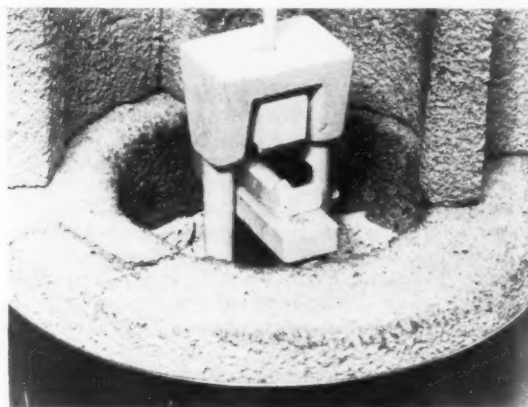
Interior view of furnace used to test flexural strength of materials at high temperatures, with specimen in place.

are bonded to the metal surface by heating the part to high temperatures. Coatings of this general type have provided extended service life for stainless steel parts. One of the Bureau coatings, NBS A–418, which was developed for the National Advisory Committee for Aeronautics, has found extensive use for the protection of certain components in jet engines.

A second Bureau coating was designed specifically for low-neutron absorption. This coating can reduce the oxidation of specimens made of an 80 Ni-20 Cr alloy by as much as 60 percent at 2,050° F. In addition, lower creep rates were observed for coated specimens under certain test conditions. The coatings were developed for use in nuclear reactors of advanced design.

Cement-type ceramic coatings have also been developed. These coatings, which have the advantage of a low-firing temperature, were developed under NACA sponsorship. They are intended to provide both short-time thermal insulation and a surface of controlled emittance for missiles and aircraft traveling at supersonic speeds.

Coatings for the refractory metals have also received attention. Ceramic and ceramic-metal compositions have been devised that give good short-time protection to molybdenum at gas temperatures up to 3,500° F. A second approach is to electroplate layers of such metals as nickel and chromium on the molybdenum surface. A thin layer of chromium is applied first, nickel is then deposited at a thickness of approximately 0.009 in. Protection of the molybdenum for periods up to 1,000 hr at 1,000° C has been achieved with layers of this type.
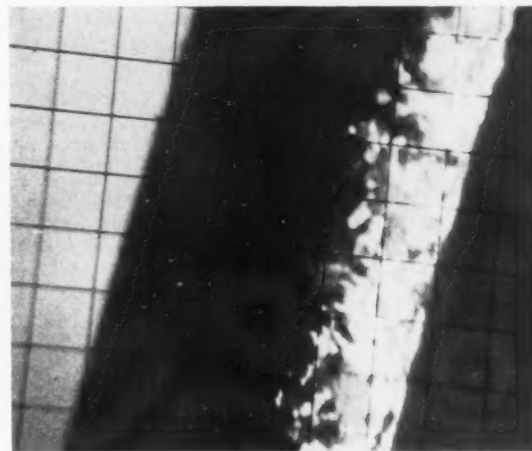
Radiation Properties of Materials

Under the sponsorship of the National Advisory Committee for Aeronautics and the Army Ballistics Missile Agency, the Bureau is studying the high-temperature radiation characteristics of enameled coatings

Decrease in diameter of nickel wire due to attack by chlorine gas, based on results obtained by a time-lapse photographic technique. Although there is some uncertainty in the diameter measurements, as indicated by the size of the circles, the rate of attack is clearly constant.
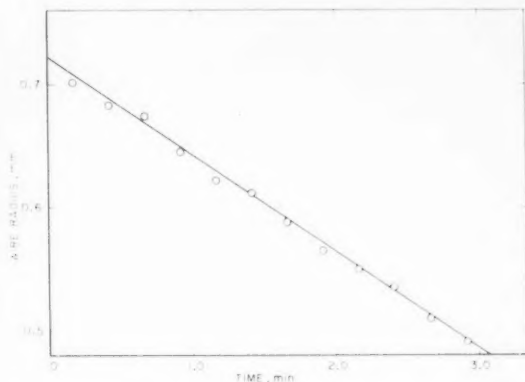
for metals. Measurements are being made by comparing, for a great number of wavelengths, the energy emitted from coated metals to the energy emitted by a laboratory blackbody furnace at the same temperature.

Aircraft or missiles operating at hypersonic speeds within the atmosphere develop high temperatures from skin friction. At these elevated temperatures, undesirable creep or corrosion of structural components can take place. Radiation is an important means of dissipating such heat. As the temperature of a hot body increases above a bright red heat, radiation will account for a major portion of the heat flow at atmospheric pressure. At high altitudes, as the density of the atmosphere decreases toward the vanishing point, the relative importance of radiation becomes even greater and ultimately becomes the only means of heat transfer.

The amount of heat transferred by radiation is determined through comparison with a blackbody. An ideal blackbody is opaque, absorbs all radiant energy incident upon its surface, and emits the maximum possible amount of radiant energy at any temperature. Well-known physical laws give the amount of such radiant

Photograph of nickel wire during a corrosive attack by chlorine gas. Such photographs were taken at 15- or 30-sec intervals to observe the progress of a gas-solid reaction.

energy as a function of temperature, and its spectral and geometric distribution. All known materials depart to some extent from these laws, and the degree of approach to blackbody properties is defined as the emittance, or, under specified conditions, the emissivity. Emittance is the ratio of the radiant energy emitted by a specimen of material to that emitted by a blackbody under similar conditions. For most materials it varies with temperature and with the wavelength over the spectrum of emitted radiation.

For computations of radiant heat transfer, accurate values of the spectral emittance of the hot body, at its

temperature, and the spectral absorptance (emittance) of the cold body, at its temperature, are required. The Bureau is now making studies to obtain such data for aircraft and missile structural and coating materials. In order to evaluate the effectiveness of enameled coatings on metals, comparisons must be made against uncoated metals. Curves of spectral emittance of two alloys, Inconel and type 321 stainless steel, have been determined over the wavelength range of approximately 1.5 to 15 μ. Specimens were subjected to one of six different treatments before evaluation: (1) Electropolishing; (2) sandblasting; (3) electropolishing followed by oxidation in air for 30 min at 1,800° F; (4) sandblasting, then oxidation in air for 30 min at 1,800° F; (5) coating with NBS ceramic coating A–418; or (6) coating with NBS ceramic coating N–143. Measurements were made at 900°, 1,200°, 1,500°, and 1,800° F.

Ceramics and Cermets

Ceramics and cermets are being used increasingly where high strength and resistance to erosion and chemical corrosion under extreme conditions of temperature are required. To realize the fullest potentialities of these materials, the Bureau is investigating such mechanical properties as strength and creep throughout the intended range of use, as well as the relationships between these properties and such parameters as grain size, porosity, temperature, minor additions, and structure.

The strength of brittle polycrystalline materials appears to vary inversely as the grain size and porosity. In the normal maturing process, the grain size usually increases as the porosity decreases. Minor additions to ceramic materials can exert a profound influence on both porosity and grain size and consequently on strength.

The investigation of some of these materials at elevated temperatures requires special equipment or techniques. For example, in the investigation of uranium dioxide or graphite, it is necessary to provide a protective atmosphere to prevent oxidation of the specimens. Also, because of the limited availability of many of the materials of interest, it has been necessary to miniaturize much of the testing equipment.

The current program in the high-temperature region includes measuring the flexural strength of uranium dioxide and thorium dioxide at temperatures up to 1,000° C. In addition, the effect of minor additions on the strength of uranium dioxide at these temperatures has been investigated. The flexural strength of single crystal aluminum oxide has been investigated up to 1,200° C, and a method developed to determine the minimum stress required to cause creep by means of the flexural strength test. Other properties, such as the modulus of elasticity, Poisson's ratio, and internal friction, are being studied on a variety of materials at temperatures as high as 1,600° C.

Heat Capacity and Conductivity

Numerous laboratories throughout the country are engaged in measuring the heat capacities (specific heats) and heat conductivities of high-temperature materials. Through its current high-temperature heat measurements program, the Bureau is contributing to this activity in two important ways. First, materials suitable as standards are chosen, and their heat conductivities and heat capacities are measured accurately. Other laboratories using simpler apparatus or more rapid methods can then use these standards to check their own measurements for constant errors that would otherwise go undetected. An example of a heat-capacity standard resulting from this program is synthetic sapphire (aluminum oxide), useful up to 900° C. This standard is now being extended up to 1,500° C. During the past few years, it has been widely used for comparisons throughout this country and abroad.

Crystallization experiments are carried out in this steel bomb at high temperatures and pressures. Temperatures up to 1,500° C can be generated from an internal electrical resistance of platinum or tungsten. Pressures up to 10,000 atm can be produced by pumping inert gases into the reaction chamber.

The second type of contribution is in making measurements on materials of fundamental or critical importance where high-temperature properties need to be known with the highest accuracy. For example, measurements of both the heat conductivity and the heat capacity of beryllium oxide were recently completed. This solid has one of the highest melting points

of nonoxidizable materials known, and is thus an important high-temperature structural material. Its relatively high heat conductivity reduces its susceptibility to thermal shock. Measuremens have also been made on the high-temperature heat capacities of 50 important metals, alloys, refractory solids, salts, and stable organic compounds. In some cases serious discrepancies among results previously obtained have been corrected. In about two dozen cases the Bureau's results have completed the information needed to calculate accurately the extent to which the materials undergo many of the most common and important chemical and physical changes at high temperatures.

Heat Flow

Two thermal properties of materials must be known to calculate heat flow. One is the thermal conductivity, which is analogous to electrical conductivity. The other property is thermal diffusivity, a measure of heat flow. When a material is not changing temperature, its thermal conductivity is a direct measure of the heat flow through the material having known temperature gradient and dimensions. When the material is changing temperature, then thermal diffusivity is calculated by dividing the thermal conductivity by the heat capacity per unit volume. Thus if the heat capacities are known, determinations of either thermal conductivity or diffusivity provide values for both of these quantities.

Very accurate measurements have been made of the thermal conductivity of pure nitrogen gas up to 500° C and 100-atm pressure. These measurements serve as standards for other laboratories to calibrate apparatus for use with other gases. Measurements have also been made of thermal conductivity of a number of solids up to 800° C. As a result of the increasing interest in measurements at higher temperatures, apparatus is being developed for extending the measurements to about 1,500° C. At the higher temperatures, determinations of thermal conductivity become increasingly difficult because they involve both absolute measurements of temperature gradient and of power. On the other hand, determinations of thermal diffusivity do not require these measurements; instead, they may involve only time interval measurements, which are much easier to make. For this reason, at the higher temperatures, only measurements of diffusivity from which conductivity values can be obtained through knowledge of heat capacities are planned. At the present time, diffusivity measurements are being made on iron, since this material has been used as a tentative standard in many laboratories. Future work is expected to include measurements on selected ceramic materials which may also serve as standards.

Standard X-ray Diffraction Patterns

Before high-temperature reactions can be understood, the substances must be identified and the structures

elucidated. X-ray diffraction provides a method for both identifying compounds and determining structure. The American Society for Testing Materials research fellowship at the Bureau greatly facilitates identification of materials by constantly reviewing the ASTM powder patterns and extending the files by preparing new patterns. Studies are also carried out by single-crystal techniques. These studies provide the structural information, such as atomic configuration, bond distances, and bond angles, that are necessary for the complete understanding of any phase changes or reactions at any temperature.

Polymers

An investigation has been undertaken to develop new polymeric materials capable of withstanding very high temperatures. This work is part of a broader program that seeks to obtain basic data on the relationship between the structure of polymers and their stability. In the course of the investigation, a number of new fluorinated organic and semi-organic compounds have been successfully synthesized. One of these materials has been used to prepare a new polymer, a fully fluorinated polyphenyl, which appears to be very stable to thermal degradation.

Preparations are now being made to study the behavior of various polymers at temperatures as high as 1,500° C. The polymers will be subjected to flash pyrolysis, and the fragments into which the polymer chain is decomposed by heat will be studied to obtain information for the further development of heat-resistant polymers.

Steels and Steel Alloys

The Bureau has undertaken a study for the Wright Air Development Center to evaluate the effects of variations in heat treatment (including refrigeration) on the mechanical properties of 17-7 PH (17% Cr-7% Ni, precipitation-hardening) stainless steel, and to determine the combinations of heat treatments that will result in optimum mechanical properties at temperatures ranging from 70° to 800° F. Further objectives are to determine the mechanisms of hardening, to identify and locate the hardening compounds, to evaluate the effects of nitrogen upon the properties of the steel, and to develop methods of eliminating or ameliorating the loss in ductility resulting from prolonged exposure at temperatures below the precipitation-hardening range.

Precipitation-hardening stainless steels, such as 17-7 PH, are now being widely used at tensile strength levels of 175,000 to 200,000 psi in aircraft where the components attain moderately elevated temperatures during flight. Up to about 800° F, these steels retain about 75 percent of their room-temperature tensile strengths.

Results of the Bureau research so far indicate that the 17-7 PH steel can be heat-treated for a tensile strength of 225,000 psi (yield of 200,000 psi) at room

temperature with sufficient ductility to be used in air-craft construction. Optimum heat treatments result in rupture life of 100 hr at a stress of 175,000 psi at 600° F or a stress of 115,000 psi at 800° F. X-ray diffraction studies of solution-annealed specimens show the presence of gamma and alpha iron and indicate the possible presence of a solid solution of titanium-carbide and titanium-nitride and a nickel-titanium-aluminum compound in addition to some unidentified constituent or compound.

As the strength of most steels decreases appreciably at elevated temperature, the development of materials having high strength at elevated temperatures becomes increasingly important. The moderately alloyed tool
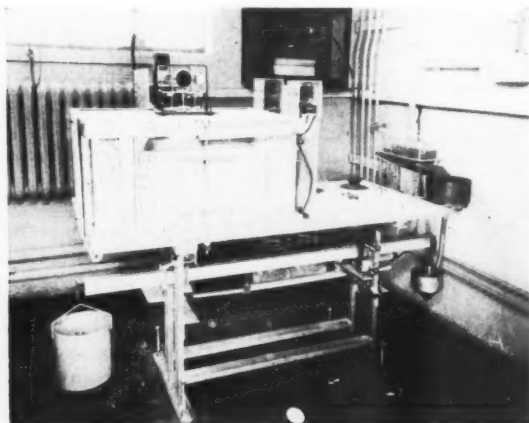
Bending test furnace used to determine creep of oxide bodies at elevated temperatures by flexural testing.

steels known as hot-work die steels may be heat-treated to very high strengths. The alloying elements normally present in these steels tend to minimize the loss of strength that otherwise would occur at temperatures up to 1,000 ° F. Because of these characteristics, four commercial 5-percent chromium hot-work die steels have been selected for study; their strength properties are being evaluated by means of tensile and stress-rupture tests at temperatures up to 1,000° F. On the basis of results obtained, experimental steels of modified analyses will be melted, fabricated, heat-treated, and tested in an effort to develop a steel having improved high-temperature strength. The results obtained to date on heat-treated specimens of some of the commercial steels show tensile strengths in excess of 200,000 psi at 1,000° F and sufficient ductility for use in aircraft components.

Stainless Steel Corrosion

Crude oil from some oil fields contains traces of a vanadium compound. This compound is not removed during refining of the oil but remains in the residue that is sold as fuel oil for ships, power plants, or tur-

bines, and forms vanadium pentoxide when burned. At temperatures above 1,100° F, the vanadium pentoxide, together with the sodium compounds always present in oil transported by tanker, forms a slag that will attack many metallic materials including high-alloy stainless steels. This corrosion results in frequent costly replacement of boiler parts.

At the request of the Navy Bureau of Ships, the Bureau is determining the minimum temperature at which the slag attack begins and the fundamental mechanism of attack of the slag on the steel. The temperature has been determined to be 1,075° F; the intensity of attack increases rapidly with increasing temperatures. The mechanism of attack is currently being investigated.

Corrosion by Liquid and Gaseous Metals

During an investigation to determine the causes of failure in riveted galvanized steel ship plates, it was found that the rivet heads frequently popped off at relatively low riveting temperatures. This was believed to have been caused by penetration of either liquid or gaseous zinc into steel stressed in tension. The Bureau is now studying the mechanism by which solid metals are attacked by a second metal of lower melting temperature in both liquid and gaseous phases.

Plans are to extend the study to higher-temperature fields and to determine the basic mechanism of such corrosive attack, including the effect of crystal orientation of the solid metal, the solid-liquid or solid-gas interface reactions, and the nature of penetration of either metallic or gaseous phases.

Time-Lapse Photography

A time-lapse photographic technique for measuring the rate at which a solid surface is attacked by corrosive gases at high temperatures has recently been developed by the Bureau in a project supported by the Atomic Energy Commission. The photographs provide a permanent record of the reaction's progress and permit accurate measurement of the rate of change of mass of the solid from its changes in dimension. The method is rapid and simple and can be applied to a considerable variety of gas-solid reactions.

Because of the severe experimental complications that arise at high temperatures, few reaction-rate studies of gas-solid reactions involving volatile products have been made even though such studies would give valuable information on the mechanism of corrosion. The manner in which the time-lapse photographic method solves many of the high-temperature problems can be seen, for example, in its application to the very rapid reaction between nickel and chlorine.

Working at temperatures from 1,100° to 1,700° K, Bureau scientists studied the reaction in which nickel and chlorine form gaseous nickel chloride. The nickel was in the form of a cylindrical wire through which a

current was passed to provide the desired temperatures. The reaction took place in a Pyrex vessel which could be evacuated to pressures as low as 10^{-6} mm of mercury; during the experiments chlorine was flowed through the vessel at various constant pressures between 0.1 and 0.5 mm of mercury.

The vessel has two windows in side arms at right angles to each other. Through one of the windows an optical pyrometer is directed towards the nickel sample to observe its temperature. Through the other, the time-lapse photographs are taken. Illumination is by radiation from the sample, and a lens system produces an image of the sample on film eight times actual size. A microswitch operated by a synchronous motor releases the shutter and advances the film at regular intervals.

From series of 10 or 15 exposures taken at intervals of 15 or 30 sec, it was established that the rate of change of sample diameter, and therefore the rate of reaction, is constant with time for the periods observed. Analysis of the data showed that the reaction rate is proportional to the chlorine pressure and extremely rapid—at least one out of every five chlorine molecule collisions with the nickel surface leads to a reaction.

Beta-Alumina Structures in Trivalent Systems

THE BUREAU, in work sponsored by the Wright Air Development Center, has been investigating a group of alkaline-earth and rare-earth oxide compounds that comprise a system of extremely high melting-point substances. Basic data on the high-temperature properties of these refractory materials are urgently needed in engineering design. An important phase of the program has been the determination of crystal structure. By this means the scientist can predict not only the behavior of the compound under study but also the properties of many structurally related substances.
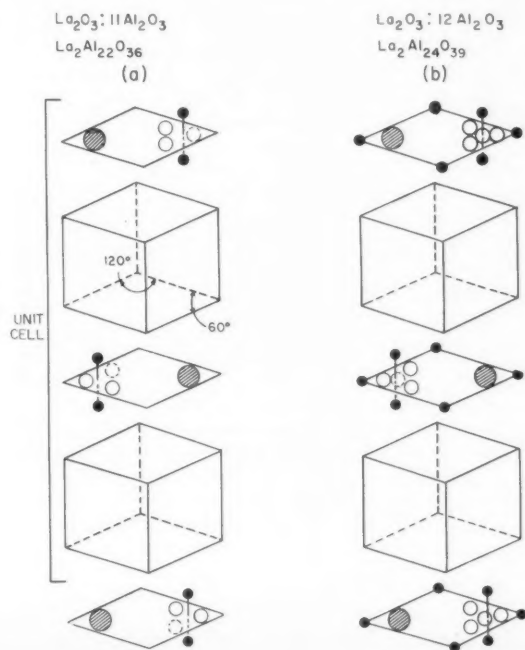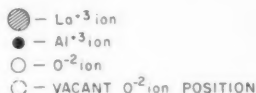
Recently, R. S. Roth [1] and S. Hasko of the Bureau staff determined the existence of a "β-alumina"-type structure in the binary lanthana-alumina (La_2O_3-Al_2O_3) system by X-ray diffraction studies. The usual form of aluminum oxide, referred to as α-alumina, crystallizes in a hexagonal rhombohedral pattern. This has a 6-sided prismatic structure with parallelogram-shaped faces. However, a hexagonal modification designated as β-alumina, has been noted in binary oxides. Structurally, this compound is entirely different from α-alumina; its only fundamental resemblance is the presence of aluminum and oxygen ions within the unit cell.

The β-alumina unit cell is based on a distorted spinel structure. But, unlike a spinel structure that has a cubic frame, the network of β-alumina is pressed into diamond-shaped blocks and has an intervening layer of metallic ions between each block. Although β-alumina-type structures are known to occur in combinations with Fe_2O_3 and with mono- and divalent oxides—which may contain various positive ions such as Na^{+1}, K^{+1}, Sr^{+2}, or Ba^{+2}—little or no work had been done on trivalent metal oxide combinations of this type. Establishment of the La_2O_3-Al_2O_3 structure should aid in understanding the ferromagnetic properties of the trivalent β-Al_2O_3 compound and related ferrites.

For the X-ray studies, seven specific proportions of lanthana to alumina were mixed and then pressed into pellets in tool steel molds. All the samples were fired in a gas furnace at an average temperature of $1,800^\circ$ C for 1 hr, when equilibrium was apparently reached. X-ray powder diffraction was then used to identify the phases.

The X-ray patterns formed were entirely different from those of α-alumina but were identified by their close resemblance to those of the β-form of SrO-Al_2O_3. The slight deviation that was observed between the two β-forms is due to the slightly greater values of the trivalent oxides' unit-cell dimensions. As the radius

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Since the definite ratio of lanthana to alumina in the β-alumina-type phase has not been established, two possible unit cell structures have been postulated. Both of these contain two rhombic-shaped blocks of aluminum and oxygen ions separated by a layer of metallic ions.

of the La^{+3} ion is somewhat larger than that of the Sr^{+2} ion, it would appear that the size of the positive ion influences the dimensional ratio of this phase. β-alumina phases formed by mono- or divalent ions with different radii have been reported to have entirely different structural parameters.

All the specimens in the experiment showed the β-alumina structure. Some contained, in addition, a small amount of α-alumina while a few samples also have some lanthanum aluminum oxide ($LaAlO_3$).

The β-Al_2O_3-type structure involving only trivalent ions as essential constituents occurs over a small range of compositions. Whether this phase is a true compound in the La_2O_3-Al_2O_3 system or whether it is a solid solution of aluminum oxide stabilized in the beta form has not been determined. The phase diagrams for either hypothesis are very similar.

Although the exact ratio of lanthana to alumina in the β-form is not known, definite ratios of monovalent and divalent oxides to β-Al_2O_3 have been established for similar compounds; the lanthana-alumina structure may be postulated on this basis. The trivalent La_2O_3-Al_2O_3 has 36 oxygen atoms, a number in between that of Na_2O-$11Al_2O_3$ and of magnetoplumbite (PbO-$6Fe_2O_3$), which have 34 and 38 oxygen atoms, respectively. Also, the total number of atoms in these two latter oxides, as calculated from the known ratios, is 58 and 64. Thus, the trivalent oxide structure might be expected to have a total quantity of 60 atoms.

Because the lanthana-to-alumina ratio has not been established, the exact distribution of the atoms within

the β-Al_2O_3 cell has not been determined. Theoretically the atoms of trivalent β-Al_2O_3 cells can assume two possible arrangements. In one configuration, the molecular ratio is 1 : 11 ($La_2Al_{22}O_{36}$). Here the La^{+3} ions occur in layers between blocks composed of 9 aluminum and 16 oxygen ions. In addition to lanthanum, oxygen and aluminum also appear in the two layers. Since 32 oxygen ions are contained in the two blocks that make up the unit cell, only two are available for each of the included layers. As there are three accessible positions, the oxygen must be randomly distributed between these loci.

For the second possibility, the ratio would be 1 : 12 or $La_2Al_{24}O_{39}$. As in the first type, lanthanum occurs in the layers between the blocks. However, the layers contain aluminum at the corners to account for two excess ions that result from the difference between the 1 : 11 and 1 : 12 ratios. Not only are all three positions in the layers occupied, but also an extra oxygen ion must be accommodated.

In both cases, oxygen must be randomly distributed among several positions. However, as all the oxygen atoms in the second arrangement are filled, there may not be enough space to accommodate the excess oxygen. Further X-ray studies on single crystal intensity are needed to establish the definite composition and structure of the β-alumina-type phase.

[1] *For further technical information, see* Beta-alumina type structure in the system lanthana-alumina, *R. S. Roth and S. Hasko, J. Am. Cer. Soc.* **41**, *146 (April 1958)*.

High-Temperature Phase Equilibrium Studies

PHASE EQUILIBRIUM STUDIES of any chemical system are concerned with the effect of the variation of environmental conditions (temperature, pressure, and composition) on the stability and chemical composition of coexisting phases (gas, liquid, or solid) of the system. Data on phase equilibrium are of vital importance for knowledge of the stability of high-temperature materials, formation of glasses, cements, metallurgical slags, and various alloys. Through use of heterogeneous equilibrium phase diagrams, experimental data on such combinations can be systematically correlated and extended to predict behavior for compositions and experimental conditions not yet explored.

In phase equilibrium studies at the Bureau,[1] increasing emphasis is now being placed on the basic properties of high-temperature ceramics and alloys. These materials usually take the form of heterogeneous systems consisting of two or more physically distinct phases separated by definite boundaries. Thus, phase diagrams can be drawn to show the condition of equilibrium between the different phases as pressure and temperature are varied. In this way seemingly unrelated data can be made to fit into a recognizable pattern, and generalizations can be made regarding all compositions in a specific system and in equivalent systems.

The phase compositions are identified experimentally by such physicochemical methods as polarizing microscopy, X-ray diffraction, electron microscopy, and infrared spectroscopy, as well as by chemical techniques. The resulting phase diagrams are used to predict for a given set of experimental conditions, the actual phases present, the compositions of the phases, and their relative concentrations under a given set of equilibrium conditions. Other data that can be obtained in this way include the temperature of initial and final melting of the compositions, components formed, information on solid solutions, extent of liquid immiscibility, and reactions occurring within the system. Such information is essential to the development of new high-temperature materials and in understanding their behavior during firing.

One of the more extensive projects is concerned with the calculation of phase-equilibrium relationships through thermodynamic and structural approaches to such problems as immiscibility, compound formation, solid solution, and melting relations. Crystal chemistry principles were applied to the quantitative interpretation of immiscibility [2] in a number of binary and ternary oxide systems.

Modifier oxides added to glass formers alter the network structure of the glass. Through analysis involv-

ing structural interpretation, it was shown that these modifiers bond to the basic network tetrahedra in one of two ways: either two small modifier cations bond to the same oxygen, or two large modifier cations bond to opposite pairs of oxygen atoms of a tetrahedron. Theoretical analysis has indicated that the type of modifier coordination is equally as important as the size of the network in determining the degree of immiscibility. The closer the separation between the cations, the greater will be the immiscibility.

Immiscibility

The boundary between the two-liquid and one-liquid region in ternary systems that exhibit immiscibility is of special interest. In phase-diagram studies involving the two glass formers, B_2O_3 and SiO_2, and a modifier oxide—of the general type CaO, BaO, PbO, and ZnO— the boundary curve bends strongly toward the modifier oxide corner. However, structural considerations indicate that with smaller modifier cations, such as MgO, the curvature would be greatly reduced. To obtain more data on this subject, the system $MgO-B_2O_3-SiO_2$ is presently being investigated.

A recently completed investigation concerns the shape of the immiscibility volume in the $BaO-B_2O_3-SiO_2$ system.[3] One aspect of this work involves the location of the postulated metastable region of immiscibility in the $BaO-SiO_2$ system. This binary system is characterized by an **S**-shaped liquidus curve which indicates a strong tendency toward two-liquid separation. However, the location of this region has never been experimentally determined. By a short projection on phase diagrams of the ternary immiscibility region into the binary system, it was shown that the critical point of the metastable curve lies about $250°$ C below the liquidus point.

Phase equilibria studies on the $MgO-GeO_2$ system,[4] which is of both theoretical and geological interest, were recently made. Previously only a limited amount of research had been conducted on general high-temperature equilibrium relations of germania (GeO_2) with other oxides. Three $MgO \cdot GeO_2$ compounds are known to occur—$1:1$, $2:1$, and $4:1$.

Germania is similar to silica in that it is a glass formerly having the same cation-oxygen ratio and tetrahedral-oxygen coordination. Because of the germanate system's possible analogy to the silicate system, comparisons of the phase diagrams of $MgO-GeO_2$ to $MgO-SiO_2$ were made. In particular, the regions of immiscibility and polymorphism were studied. The extent of immiscibility in corresponding silicate and germanate systems is believed to be about the same. Since the $MgO-GeO_2$ system represents the maximum extent of immiscibility expected with divalent modifier oxides, it is of special interest. Then, too, by correlation with germanate structural forms, scientists may locate corresponding polymorphic forms in the $MgO-SiO_2$.

Previous workers have proposed three polymorphs for $MgO-SiO_2$: A low temperature called Enstatite; an intermediate-temperature, Clinoenstatite; and a high temperature, Protoenstatite. The present belief is that the Protoenstatite is the stable high-temperature polymorph but cannot be successfully quenched. When cooled to room temperature this form becomes unstable and reverts to Clinoenstatite. It was hoped that studying the $MgO-GeO_2$ system might reveal the stable structural types for the silicates. However, in the germanate studies only the Clinoenstatite in a stable form was observed.

Other dissimilarities exist between the two systems. The $1:1$ $MgO-GeO_2$ melts congruently (i. e., forms a liquid of the same composition) at $1,700° \pm 20°$ C, in contrast to $MgO-SiO_2$ which melts incongruently at a much lower temperature, $1,557°$ C. Also, whereas the two-liquid formation of the silicate system occurs at $1,693°$ C, 18 deg below the melting point of SiO_2, the corresponding germanate formation occurs at $1,500°$ C, which is almost 370 deg above the melting point of GeO_2.

Phase-diagram studies of the binary $SrO-GeO_2$ system were recently begun in continuation of germanate studies with modifier oxides.

Piezoelectricity

Investigations are in progress of all the ternaries in the $PbO-Nb_2O_5-ZrO_2-TiO_2$ system as well as the binary
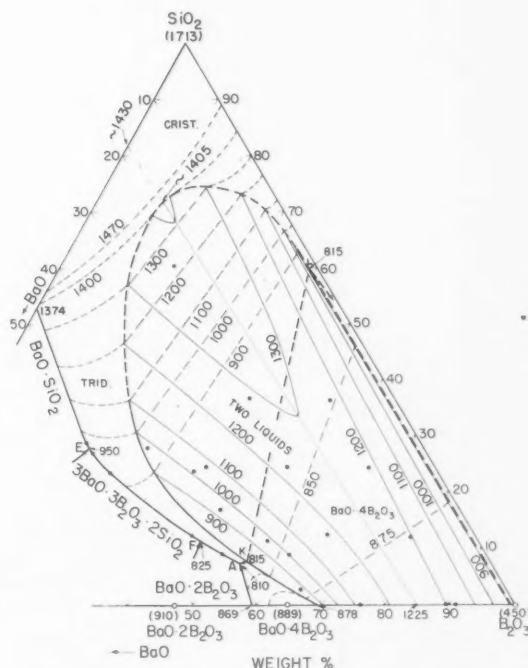
Shape of liquid immiscibility volume in the system $BaO-B_2O_3-SiO_2$. Isotherms in the surface of the dome are shown as light solid lines. The critical solution curve is shown as a light solid line approximately parallel to the $B_2O_3-SiO_2$ boundary.

PbO-Nb₂O₅. The four-component system is of particular significance because of promising piezoelectric properties. Since, in general, little data have been available on combinations of binary systems involving lead, isothermal studies at the Bureau centered around the PbO-ZrO₂ and PbO-TiO₂ binaries. In a 1:1 ratio, the binary titanate is known to be ferroelectric while the binary zirconate is antiferroelectric. However, the solid solution between these two is piezoelectric. Work at the Bureau concerned suitable conditions for producing the piezoelectric material from the solid solution.

Although most piezoelectric materials are single-oxide components, a combination in polycrystalline form may also have this characteristic if ferroelectric. PbO·Nb₂O₅ is one such compound. However, the ferroelectric phase in this case is not stable in itself; impurities of ZrO₂ or TiO₂ are needed to stabilize the phase.

The 1:1 ratio of PbO·Nb₂O₅ (PbNb₂O₆) has a reversible phase transformation at about 1,250° C and changes at this temperature from a rhombohedral to a tetragonal structure. This high-temperature polymorph of PbNb₂O₆ can be quenched, and instead of reverting to the rhombohedral structure, it undergoes an additional transformation to the orthorhombic ferroelectric form. This ferroelectric is only metastable, apparently having no equilibrium region in the pure binary PbO-Nb₂O₅. When ZrO₂ and/or TiO₂ are present in quantities as low as 1 mole percent, the rhombohedral form is completely eliminated in favor of the ferroelectric; with one-half mole percent, the rhombohedral and ferroelectric phases both appear, while with two-tenths of a mole percent complete phase transformations can be made to take place. This indicates that there is no place in the PbNb₂O₆-ZrTiO₄ phase diagram where the rhombohedral structure will form except in the very pure state. Whether the ferroelectric form is actually stabilized by the impurities, or whether it is made more metastable for the duration of the experiments has not been determined.

In order to examine further the nature of the compounds occurring in the PbO-Nb₂O₅ system, phases in BaO-Nb₂O₅, SrO-Nb₂O₅, PbO-Ta₂O₅, BaO-Ta₂O₅, and SrO-Ta₂O₅ were separately studied. BaO-Nb₂O₅ forms a structure closely related to the low-temperature rhombohedral form of PbO-Nb₂O₅, while PbO-Ta₂O₅ has a structure very similar to the high-temperature form of PbNb₂O₆. The X-ray pattern for the latter appears to be tetragonal, but evidence of ferroelectricity indicates that it is actually orthorhombic. BaO-Ta₂O₅ and SrO-Ta₂O₅ also have temperature polymorphs similar to the orthorhombic structure of BaNb₂O₆. The high-temperature polymorph of SrTa₂O₆ is similar to the ferroelectric modification of PbNb₂O₆.

Rare Earths

Work has recently been undertaken on the relatively unexplored rare-earth oxide systems, including lanthana-alumina (La₂O₃-Al₂O₃) and dysprosia alumina

(Dy₂O₃-Al₂O₃). Comparatively little research has been conducted on rare earths because of their previous unavailability. However, in obtaining purified thorium for nuclear reactions, rare earths are extracted as impurities. Oxides of these elements are particularly important because of their refractory and ferromagnetic properties. For the present project, dysprosium was chosen for study because of its similarity to yttrium, which is not a rare earth and which has been studied to some extent. To obtain further information on the ternary La₂O₃-Al₂O₃-Dy₂O₃ system, phase diagrams of the three binary systems are being studied. Within the La₂O₃-Al₂O₃ system, two structures have been noted; one is a rhombohedral distorted perovskite (ABO₃) form with a 1:1 ratio and the other is a β-alumina form with a 1:11 or 1:12 ratio. (See page 119 of this issue.) Melting point data are now being gathered on these structures.

Within the Al₂O₃-Y₂O₃ system, a perovskite (orthorhombic distorted) structure of 1:1 ratio and a garnet structure at a 5:3 ratio have been found. By substitut-
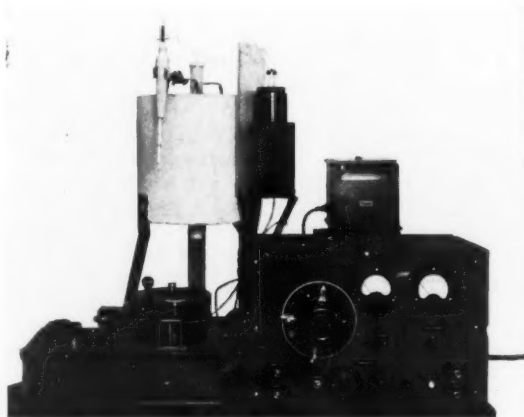
Self-adjusting controller (right) which maintains precise temperature control of a quenching furnace (background).

ing Dy₂O₃ for the Y₂O₃, the relationship between these forms is now being examined. Within the La₂O₃-Y₂O₃ system a perovskite structure with a 1:1 ratio is present only below 1,500° C. A β-type structure is noted above this temperature and solid solutions of the single phases occur for all ratios.

Alloys

To understand and predict the characteristics of alloys, phase diagrams are constructed to show melting ranges, structural changes occurring at various temperatures, intermetallic compounds, and solubility-temperature relationships.

A large proportion of the commercial heat-resistant alloys contain chromium, iron, molybdenum, cobalt,

and nickel. To provide phase diagrams on the alloys, in which extraneous elements—such as carbon, oxygen, and nitrogen—are held to a minimum, diagrams of binary, ternary, and quaternary systems of Cr-Fe-Mo-Ni are being studied. Because impurities in alloys may have either a detrimental or beneficial effect on desirable mechanical properties, a knowledge of the phase reactions in the high-purity alloys may provide a basis for studying and understanding the complex reactions resulting from the addition of these extraneous elements.

An important phase of this work deals with the 17:7 chromium-nickel alloy. Under appropriate heat treatments, this alloy develops relatively high strengths at room temperature. The commercial alloy also contains about 1.25 percent of aluminum and small amounts of carbon and nitrogen. How these extra elements act to influence the precipitation-hardening reactions of the commercial alloy is not yet known. However, the possibility of precipitation of a hard, brittle intermetallic compound has been suggested by phase diagrams.

In research sponsored by the Atomic Energy Commission on the alloys of uranium with the platinum metals (platinum, rhodium, ruthenium, osmium, and iridium), the equilibrium diagram of the platinum-uranium system was recently brought to completion. Much of the exploratory work on the other platinum metals has been done, and progress has been made on the rather complex uranium-palladium system.

Type 431 stainless steel (16% Cr, 2% Ni) is frequently used for aircraft components but it appears to vary from heat to heat as regards toughness. The normal response of this type of steel to heat treatment produces a combination of relatively high strength and ductility and thus makes its use highly desirable in the aircraft industry, provided the occasional heats of low ductility can be prevented. An accurate equilibrium diagram, needed for a better understanding of this steel, is now being established.

Controller

In high-temperature phase studies, it is important to maintain a sample at a desired temperature until equilibrium is reached. For this purpose, an improved, self-adjusting, bridge-type controller which is suitable for precise temperature control of a quenching furnace has been developed. With this controller, a given temperature can be held constant to within 0.3° C. Since the platinum-rhodium winding serves both as a heater and as a sensing element, there is virtually no time delay between a change in power input and a change in temperature.

Based on the Wheatstone bridge principle, the instrument produces a resistance change for every variation in temperature. The deviation which results causes the controller to readjust the power input by means of a variable autotransformer. Thus, the power to the furnace is continuously adjusted to maintain the desired resistance. The apparatus is made of commercial components, and is simple to operate on readily available a-c current.

[1] *Many of the Bureau's phase diagrams appear in the* Phase diagrams for ceramicists, *by E. M. Levin, H. F. McMurdie, and F. T. Hall, copyright 1956, Am. Cer. Soc., Columbus, Ohio.*

[2] Structural interpretation of immiscibility in oxide systems, *NBS Tech. News Bul.* **41**, 169 *(November 1957). For further technical details, see* Structural interpretation of immiscibility in oxide systems, *by E. M. Levin and S. Block, I.* Analysis and calculation of immiscibility, *J. Soc. Ceram.* **40**, 95 (1957), *II.* Coordination principles applied to immiscibility, *J. Soc. Ceram.* **40**, 113 (1957), *III.* Effect of alkalies and alumina in ternary systems, *J. Am. Ceram. Soc.* **41**, 49 (1958).

[3] Shape of liquid immiscibility volume in the system barium oxide-boric oxide-silica, *by E. M. Levin and G. W. Cleek, J. Am. Ceram. Soc.* (in press).

[4] The system magnesium oxide-germanium dioxide, *C. Robbins and E. M. Levin* (in press).

Publications of the National Bureau of Standards

Periodicals

Journal of Research of the National Bureau of Standards, Volume **60**, No. 5, May 1958 (RP2857 to RP2866 incl.), 60 cents. Annual subscription $4.00, $1.25 additional for foreign mailing.

Technical News Bulletin, Volume **42**, No. 5, May 1958. 10 cents.

Basic Radio Propagation Predictions for August 1958. Three months in advance. CRPL-D165. Issued May 1958. 10 cents. Annual subscription $1.00, 25 cents additional for foreign mailing.

Research Papers

Journal of Research, Volume 60, No. 5, May 1958. 60 cents.

RP2857. Forces on cylinders and plates in an oscillating fluid. Garbis H. Keulegan and Lloyd H. Carpenter.

RP2858. Reaction of portland cement with carbon dioxide. Charles M. Hunt, Vernon Dantzler, Lewis A. Tomes, and Raymond L. Blaine.

RP2859. Average energy of sulfur-35 beta decay. Howard H. Seliger, Wilfrid B. Mann, and Lucy M. Cavallo.

RP2860. Effect of structure on the thermal decomposition of polymers. Leo A. Wall and Roland E. Florin.

RP2861. Comparison of theoretical and empirical relations between the shear modulus and torsional resonance frequencies for bars of rectangular cross section. Sam Spinner and Rudolph C. Valore, Jr.

RP2862. Specific volume and degree of crystallinity of semicrystalline poly(chlorotrifluoroethylene), and estimated specific volumes of the pure amorphous and crystalline phases. John D. Hoffman and James J. Weeks.

RP2863. Heat and ultraviolet aging of poly(vinyl chloride). Charles F. Bersch, Mary R. Harvey, and Bernard G. Achammer.

RP2864. Determination of water vapor from the change in electrical resistance of a hygroscopic film. Elmer R. Weaver, Ernest E. Hughes, and Albert W. Diniak.

RP2865. Improved bridge method for the measurement of core losses in ferromagnetic materials at high flux densities. William P. Harris and Irvin L. Cooter.

RP2866. Stress-strain relationships in yarns subjected to rapid impact loading: 5. Wave propagation in long textile yarns impacted transversely. Jack C. Smith, Frank L. McCrackin, and Herbert F. Schiefer.

TECHNICAL NEWS BULLETIN

Contents

NBS Publications (*continued*)

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Dielectric properties of titania or tin oxide containing varying proportions of rare-earth oxides. S. Marzullo and E. N. Bunting. J. Am. Ceram. Soc. **41**, No. 1, 40–41 (Jan. 1958).

Elasticity, strength, and other related properties of some refractory castables. S. J. Schneider and L. E. Mong. J. Am. Ceram. Soc. **41**, No. 1, 27–32 (Jan. 1958).

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A field emitter point projection X-ray microscope. L. Marton, R. A. Schrack, and R. B. Placious. X-ray Microscopy and Microradiography, 287–292 (Nov. 1957).

Fracture phenomena and molecular weight in polymethyl methacrylate. Sanford B. Newman and Irvin Wolock. J. Appl. Phys. **29**, No. 1, 49–52 (Jan. 1958).

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Radiation exposure and the use of radioisotopes. Lauriston S. Taylor. Impact of Sci. on Soc. **8**, No 4 (1957).

Patents

(The following United States Patents have been granted to NBS inventors during the quarter ending March 31, 1958, and have been assigned to the U. S. Government as represented by the Secretary of the Department noted in parentheses.)

No. 2,819,940. January 14, 1958. Drive controls for magnetic recorder-reproducer. John R. Sorrells (Commerce).

No. 2,820,900. January 21, 1958. Magnetron overload protection circuit. Robert K-F. Scal (Navy).

No. 2,821,280. January 28, 1958. Feed mechanism. Haaren A. Miklofsky (Navy).

No. 2,821,856. February 4, 1958. Rapid gas-sampling valve. William J. Levedahl (Commerce).

No. 2,824,060. February 18, 1958. Bearing compositions containing polytetrafluoroethylene and polytrifluorochloroethylene. Hobart S. White (Navy).

No. 2,824,218. February 18, 1958. Automatic radio control for clocks. Theodore R. Gilliland (Commerce).

No. 2,826,079. March 11, 1958. Automatic coin weighing machine. Milton L. Kuder, Ervin C. Palasky, Saul R. Gilford, and Maurice L. Greenough (Commerce).

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